



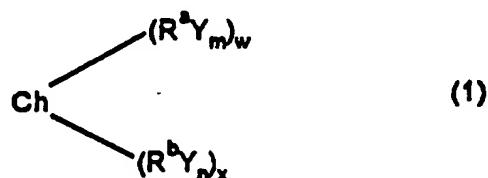
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(54) Title: DYE DIFFUSION THERMAL TRANSFER PRINTING

(57) Abstract

A thermal transfer dye sheet comprises a substrate having a coating comprising a dye of formula (1) wherein: Ch is a chromogen; R^a and R^b each independently is a spacer group; Y is an interactive functional group; w and x each independently is 0 or an integer equal to or greater



than 1; and m and n each independently is an integer equal to or greater than 1, provided that w and x are not both equal to zero and when one of w or x is 0 at least one of m and n is equal to or greater than 2. A thermal transfer dye sheet/receiver sheet combination in which the dye sheet comprises a coating comprising a dye or mixture of dyes of formula (1) and in which the receiver sheet contains a polymer having at least one group capable of interacting with Y.

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Dye Diffusion Thermal Transfer PrintingIntroduction

5 This invention relates to dye diffusion thermal transfer printing (DDTTP or D2T2 printing, D2T2 is a trade mark of Imperial Chemical Industries PLC), especially to a dye sheet carrying a dye or a dye mixture which has an improved print stability and to a transfer printing process in which the dye or the dye mixture is transferred from the transfer sheet to a receiver sheet by the application of heat.

10 It is known to print woven or knitted textile material by a thermal transfer printing (TTP) process. In such a process a sublimable dye is applied to a paper substrate (usually as an ink also containing a resinous or polymeric binder to bind the dye to the substrate until it is required for printing) in the form of a pattern, to produce a transfer sheet comprising a paper substrate printed
15 with a pattern which it is desired to transfer to the textile. Substantially all the dye is then transferred from the transfer sheet to the textile material, to form an identical pattern on the textile material, by placing the patterned side of the transfer sheet in contact with the textile material and heating the sandwich, under light pressure from a heated plate, to a temperature from 180-220°C for a period of 30-120 seconds.

20 As the surface of the textile substrate is fibrous and uneven it will not be in contact with the printed pattern on the transfer sheet over the whole of the pattern area. It is therefore necessary for the dye to be sublimable and vaporise during passage from the transfer sheet to the textile substrate in order for dye to be transferred from the transfer sheet to the textile substrate over the whole of the pattern area.

25 As heat is applied evenly over the whole area of the sandwich over a sufficiently long period for equilibrium to be established, conditions are substantially isothermal, the process is non-selective and the dye penetrates deeply into the fibres of the textile material.

In DDTTP, a transfer sheet is formed by applying a heat-transferable dye (usually in the
30 form of a solution or dispersion in a liquid also containing a polymeric or resinous binder to bind the dye to the substrate) to a thin (usually <20 micron) substrate having a smooth plain surface in the form of a continuous even film over the entire printing area of the transfer sheet. Dye is then selectively transferred from the transfer sheet by placing it in contact with a material having a smooth surface with an affinity for the dye, hereinafter called the receiver sheet, and selectively
35 heating discrete areas of the reverse side of the transfer sheet for periods from about 1 to 20 milliseconds (msec) and temperatures up to 300C, in accordance with a pattern information signal, whereby dye from the selectively heated regions of the transfer sheet diffuses from the transfer sheet to the receiver sheet and forms a pattern thereon in accordance with the pattern in which heat is applied to the transfer sheet. The shape of the pattern is determined by the number

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and location of the discrete areas which are subjected to heating and the depth of shade in any discrete area is determined by the period of time for which it is heated and the temperature reached.

Heating is generally, though not necessarily, effected by a line of heating elements, over which the receiver and transfer sheets are passed together. Each element is approximately square
5 in overall shape, although the element may optionally be split down the centre, and may be resistively heated by an electrical current passed through it from adjacent circuitry. Each element normally corresponds to an element of image information and can be separately heated to 300°C to 400°C, in less than 20 msec and preferably less than 10 msec, usually by an electric pulse in response to a pattern information signal. During the heating period the temperature of an element
10 will rise to about 300-400°C over about 5-8 msec. With increase in temperature and time more dye will diffuse from the transfer sheet to the receiver sheet and thus the amount of dye transferred onto, and the depth of shade at, any discrete area on the receiver sheet will depend on the period for which an element is heated while it is in contact with the reverse side of the transfer sheet.

15 As heat is applied through individually energised elements for very short periods of time the process is selective in terms of location and quantity of dye transferred and the transferred dye remains close to the surface of the receiver sheet.

As an alternative heating may be effected using a light source in a light-induced thermal transfer (LITT or L2T2 printing) printer where the light source can be focused, in response to an
20 electronic pattern information signal, on each area of the transfer sheet to be heated. The heat for effecting transfer of the dye from the transfer sheet is generated in the dyesheet which has an absorber for the inducing light. The absorber is selected according to the light source used and converts the light to thermal energy, at a point at which the light is incident, sufficient to transfer the dye at that point to the corresponding position on the receiver sheet. The inducing light usually has
25 a narrow waveband and may be in the visible, infra-red or ultra violet regions although infra- red emitting lasers are particularly suitable.

It is clear that there are significant distinctions between TTP onto synthetic textile materials and DDTTP onto smooth polymeric surfaces and thus dyes which are suitable for the former process
30 are not necessarily suitable for the latter.

In DDTTP it is important that the surfaces of the transfer sheet and receiver sheet are even so that good contact can be achieved between the printed surface of the transfer sheet and the receiving surface of the receiver sheet over the entire printing area because it is believed that the dye is transferred substantially by diffusion in the molten state in condensed phases. Thus, any
35 defect or speck of dust which prevents good contact over any part of the printing area will inhibit transfer and lead to an unprinted portion on the receiver sheet on the area where good contact is prevented, which can be considerably larger than the area of the speck or defect. The surfaces of the substrate of the transfer and receiver sheets are usually a smooth polymeric film, especially of a polyester, which has some affinity for the dye.

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Important criteria in the selection of a dye for DDTTP are its thermal properties, fastness properties, such as light fastness, and facility for transfer by diffusion into the substrate in the DDTTP process. For suitable performance the dye or dye mixture should transfer evenly and rapidly, in proportion to the heat applied to the transfer sheet so that the amount transferred to the receiver sheet is proportional to the heat applied. After transfer the dye should preferably not migrate or crystallise and should have excellent fastness to light, heat, rubbing, especially rubbing with a oily or greasy object, e.g. a human finger, such as would be encountered in normal handling of the printed receiver sheet and when in contact with plastics materials containing plasticisers, particularly poly(vinyl chloride) e.g. by being placed in a wallet of such material.

- 10 . The dye should be sufficiently mobile to migrate from the transfer sheet to the receiver sheet at the temperatures employed, 100-400°C, in the short time-scale, generally <20 msec. Many potentially suitable dyes are also not readily soluble in the solvents which are commonly used in, and thus acceptable to, the printing industry; for example, alcohols such as *i*-propanol, ketones such as methyl ethyl ketone (MEK), methyl *i*-butyl ketone (MIBK) and cyclohexanone, ethers such as
- 15 tetrahydrofuran and aromatic hydrocarbons such as toluene. The dye can be applied as a dispersion in a suitable medium or as a solution in a suitable solvent to the substrate from a solution. In order to achieve the potential for a high optical density (OD) on the receiver sheet it is desirable that the dye should be readily soluble or readily dispersable in the ink medium. It is also important that a dye which has been applied to a transfer sheet from a solution should be resistant to crystallisation so
- 20 that it remains as an amorphous layer on the transfer sheet for a considerable time. Crystallisation not only produces defects which prevent good contact between the transfer receiver sheet but gives rise to uneven prints.

The following combination of properties is highly desirable for a dye which is to be used in DDTTP:-

Ideal spectral characteristics (narrow absorption curve and high tinctorial strength)

Correct thermochemical properties (high thermal stability and efficient transferability with heat).

High optical densities on printing.

- 30 Good solubility in solvents acceptable to printing industry: this is desirable to produce solution coated dyesheets alternatively good dispersibility in acceptable media is desirable to produce dispersion coated dyesheets.

Stable dyesheets (resistant to dye migration or crystallisation).

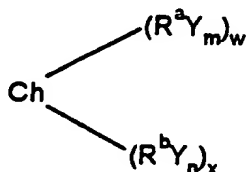
- 35 Stable printed images on the receiver sheet (resistant to heat, migration, crystallisation, grease, rubbing and light).

DDTTP is used for printing images on suitable substrates.

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The achievement of good light fastness in DDTTP is extremely difficult because of the unfavourable environment of the dye, close to the surface of the receiver sheet. To preserve an image on a receiver sheet it is important to minimise migration and/or crystallisation of the dye. An objective of the present invention is to overcome the above problems by providing a convenient means of enhancing print stability and minimising migration and crystallisation of dyes in DDTTP without the disadvantage of substantially changing the absorption maximum of the dye.

According to the present invention there is provided a thermal transfer dye sheet comprising a substrate having a coating comprising a dye of Formula (1):



Formula (1)

wherein

Ch is a chromogen;

R^a and R^b each independently is a spacer group;

Y is an interactive functional group;

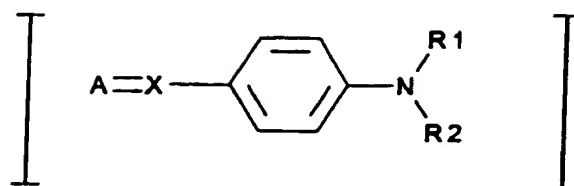
w and x each independently is 0 or an integer equal to or greater than 1; and

m and n each independently is an integer equal to or greater than 1, provided that w and x are not both equal to zero and when one of w or x is 0 at least one of m and n is equal to or greater than 2.

In this specification, the term "chromogen" is defined as meaning the arrangement of atoms which governs the absorbance of electromagnetic radiation by the dye molecule and particularly in the case of visible radiation, the arrangement of atoms which causes the dye molecule to be coloured.

The chromogen represented by Ch is preferably an optionally substituted group of Formula (2):

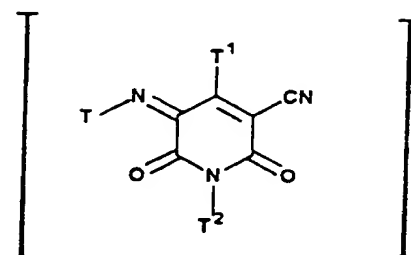
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Formula (2)

or an optionally substituted group of Formula (2B):

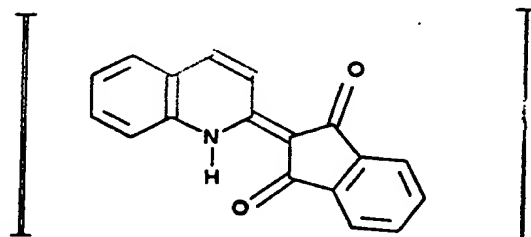
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Formula (2B)

20 in which T is A^1-NH or optionally substituted phenyl (such as optionally substituted mono- or dialkylaminophenyl), T^1 is optionally substituted C_{1-12} -alkyl or optionally substituted aryl, and T^2 is optionally substituted alkyl; or an optionally substituted group of Formula (3):

25



30

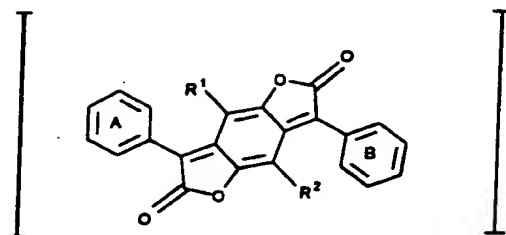
Formula (3)

or an optionally substituted group of Formula (4):

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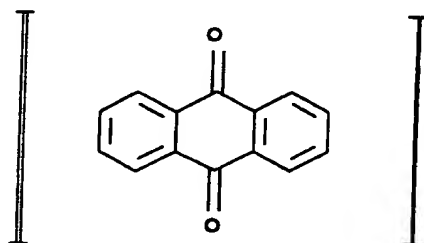


Formula (4)

10 in which rings A and B are optionally substituted and R¹ and R² each independently is H, alkyl, alkoxy or halogen;

or an optionally substituted group of Formula (5):

15



20

Formula (5)

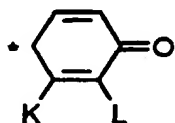
in which

25

X is -C(R)- or N and R is H, CN or COOalkyl; and

A is A'-N in which A' is the residue of a diazotisable aromatic or heteroaromatic amine or A is selected from an optionally substituted group of Formula (6):

30



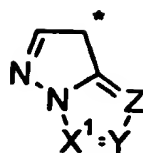
Formula (6)

35 in which K and L each independently is -CN, NO₂, -Cl, -F, -Br, C₁₋₆ alkyl, C₁₋₆ alkoxy, -NHCOC₁₋₆ alkyl, -NHCophenyl, -NHSO₂ alkyl, NHSO₂phenyl or aryloxy, or K and L together with the carbon atoms to which they are attached form a 5- or 6-membered carbocyclic or heterocyclic ring ;or

an optionally substituted group of Formula (7):

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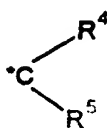
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Formula (7)

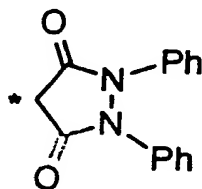
wherein X^1 , Y and Z each independently is N or C- R^3 in which R^3 is -H, -CN alkyl, alkoxy, cycloalkyl, aryl, aralkyl, aryloxy or amino; or

an optionally substituted group of Formula (8):

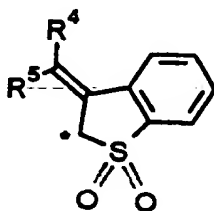


Formula (8)

wherein R^4 and R^5 each independently is an electron withdrawing group or R^4 and R^5 may be joined form a heterocyclic ring such as;



or an optionally substituted group of Formula (9):

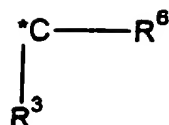


Formula (9)

wherein R^4 and R^5 are as hereinbefore defined; or an optionally substituted group of Formula (10):

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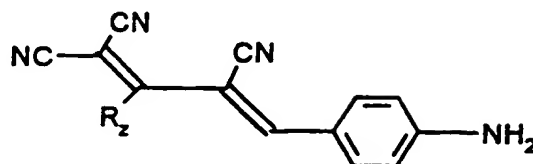


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Formula (10)

wherein R^3 is as hereinbefore defined and R^6 is alkenyl or

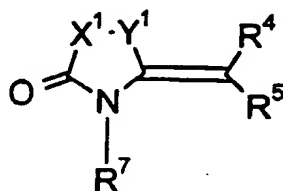
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15 wherein R^4 is NH_2 , phenyl or succinamido;

or an optionally substituted group of Formula (11):

20



Formula (11)

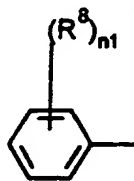
25 in which X^1 and Y^1 are both C and R^4 and R^5 are as hereinbefore defined and R^7 is -H, alkyl or aryl,

where * shows the point of attachment to the double bond in Formula (2).

A^1 is preferably selected from phenyl, naphthyl, thiazolyl, isothiazolyl, benzothiazolyl, benzoisothiazolyl, pyrazolyl, thiadiazolyl, imidazolyl, thienyl, pyridyl and pyridoisothiazolyl each of 30 which may be optionally substituted.

Where A^1 is phenyl it is preferably of the Formula (12):

35



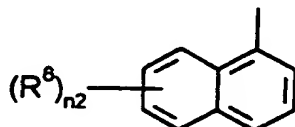
Formula (12)

wherein:

R^8 is -H, optionally substituted alkyl, optionally substituted alkoxy, -NO₂, -CN, -CF₃, -SCN, halogen, alkoxyalkyl, -COalkyl, -OCOalkyl, -COOalkyl, -SO₂NH₂, -SO₂F, -SO₂Cl, -CONH₂, -COF, -COCl, -SO₂alkyl, -CONH(alkyl), -CON(alkyl)₂, -SO₂N(alkyl)₂, -Salkyl, -Sphenyl; and

n^1 is an integer from 1 to 5.

Where A¹ is naphthyl it is preferably a naphth-1-yl of the Formula (13):



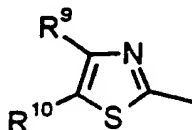
Formula (13)

wherein:

R^8 is as hereinbefore defined; and

n^2 is an integer from 1 to 4.

Where A¹ is thiazolyl it is preferably a thiazol-2-yl of the Formula (14):



Formula (14)

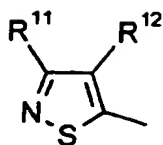
wherein:

R^9 is -H or optionally substituted alkyl, optionally substituted alkoxy, optionally substituted aryl, halogen or -Salkyl; and

R^{10} is -H, optionally substituted alkyl, alkenyl, -CN, -NO₂, -SO₂alkyl, -COOalkyl, halogen or -CHO.

Where A¹ is isothiazolyl it is preferably an isothiazol-5-yl of the Formula (15):

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Formula (15)

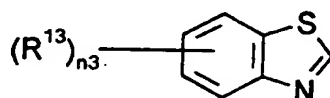
wherein:

10 R^{11} is -H, optionally substituted alkyl, optionally substituted aryl, -SO₂alkyl, -Salkyl, -Saryl or halogen; and

R^{12} is -H, -CN, -NO₂, -SCN or -COOalkyl.

Where A¹ is benzothiazolyl it is preferably a benzothiazol-2-yl of the Formula (16):

15



Formula (16)

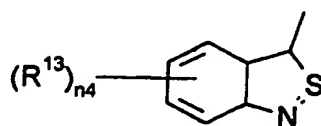
20 wherein:

R^{13} is -H, -SCN, -NO₂, -CN, halogen, optionally substituted alkyl, optionally substituted alkoxy, -COOalkyl, -OCOalkyl or -SO₂alkyl; and

n^3 is from 1 to 4.

25

Where A¹ is benzoisothiazolyl it is preferably a benzoisothiazol-3-yl of the Formula (17):



30

Formula (17)

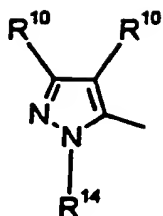
wherein:

35 R^{13} is as hereinbefore defined; and

n^4 is from 1 to 4.

Where A¹ is pyrazolyl it is preferably a pyrazol-5-yl of the Formula (18):

11



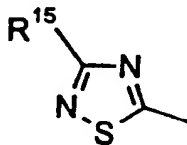
Formula (18)

wherein:

each R^{10} is independently as hereinbefore defined; and

R^{14} is -H, optionally substituted alkyl or optionally substituted aryl.

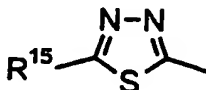
Where A' is thiadiazolyl it is preferably a 1,2,4-thiadiazol-5-yl of Formula (19):



Formula (19)

wherein:

R^{15} is -Salkyl, -Saryl, -SO₂alkyl or halogen or is a 1,3,4-thiadiazol-5-yl of Formula (20)



Formula (20)

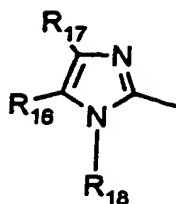
wherein:

R_{15} is as hereinbefore defined.

Where A' is imidazolyl it is preferably an imidazol-2-yl of the Formula (21):

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Formula (21)

wherein:

10

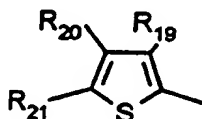
R_{18} is -CN, -CHO, -CH=C(CN)₂ or -CH=C(CN)(COOalkyl);

R_{17} is -CN or -Cl; and

R_{18} is -H or optionally substituted alkyl.

15

Where A' is thienyl it is preferably a thien-2-yl of the Formula (22):



20

Formula (22)

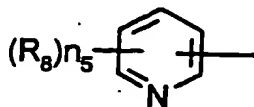
wherein:

R_{19} is -NO₂, -CN, alkylcarbonylamino or alkoxy carbonyl;

25 R_{20} is -H, halogen, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted aryl or -Salkyl; and

R_{21} is -H, optionally substituted alkyl, -CN, -NO₂, -SO₂alkyl, -COOalkyl, halogen, -CH=C(CN)₂ or -CH=C(CN)(COOalkyl).

30 Where A' is pyridyl it is preferably a pyrid-2-yl, pyrid-3-yl or pyrid-4-yl of the Formula (23):



35

Formula (23)

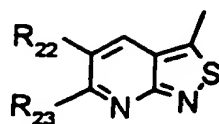
wherein:

R_8 is as hereinbefore defined; and

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n_3 is from 1 to 4.

Where A' is pyridoisothiazolyl it is preferably a pyridoisothiazol-3-yl of the Formula (24):



Formula (24)

wherein:

R_{22} is -CN or -NO₂; and

15 R_{23} is optionally substituted alkyl.

According to a preferred aspect of the invention, the chromogen contains an α -branched, N-alkyl group.

The inclusion of such a group increases the resistance to fading under the influence of light.

20 The spacer groups represented by R^a and R^b may be any groups capable of carrying one or more interactive functional groups (Y) and minimising steric and electronic effects of the Y group and thereby minimising any changes in the absorption characteristics of the chromogen group Ch and thus shade which the Y group would otherwise cause.

25 Preferably the spacer groups each comprise an atom or group of atoms connected to the chromagen by at least one sigma bond and to the interactive group by at least one sigma bond.

The spacer groups may contain at least one of a carbon, silicon or sulphur atom, preferably two carbon atoms and more preferably from three to ten carbon atoms.

30 The interactive functional group represented by Y are such that the Y groups on different dye molecules may be interact with each other to form dye complexes of larger size and thus of lower mobility and/or the Y groups may interact with a dye receptive polymer on the receiver sheet. In the dyes of Formulae (1) to (5) the Y groups may be the same or different and the R^a and R^b may carry one more Y groups. The interactions between different Y groups or between the Y groups and the dye receptive polymer produces an image on the receiver sheet which is resistant to 35 crystallisation and migration of the dyes is minimised. The Y groups are preferably selected from OH, NH₂, NHR, NR₂, COOH, CONH₂, NHCOR, CONHR, SO₂NH₂, SO₂NHR, SO₃H, NHCONH₂, NHCONHR, =NOH, and PO₃H, in which R is selected from -CN, NO₂, -Cl, -F, -Br, -C₁₋₆alkyl, C₁₋₆alkoxy, -NHCOC₁₋₆alkyl, -NHCOPhenyl, -NHSO₂alkyl, -NHSO₂phenyl or aryloxy, more preferably from the groups having at least one H atom.

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Dyes with low melting points are generally unsuitable for use in DDTTP because they migrate within the receiver sheet or retransfer to materials to which they are in contact. It is surprising therefore that dyes of the present invention which have melting points as low as 20° C produce images on the receiver sheets which do not migrate.

5 According to a preferred feature of the invention, the dye sheet contains a dye of Formula (1) which is liquid at room temperature or which has a melting point in the range from 20°C to 200°C, preferably in the range from 20° C to 150°C.

The dyes for use in the dye sheet of the invention may be prepared by conventional
10 methods such as those described in EP285665, EP400706, EP483791. For more detailed information on the preparation of the dyes disclosed herein, reference may be made to the co-pending PCT application in the name of Zeneca Limited and claiming priority from GB 9508810.0.

The Coating

15 The coating suitably comprises a binder together with a dye or mixture of dyes of Formula (1). The ratio of binder to dye is preferably at least 0.7:1 and more preferably from 1:1 to 4:1 and especially preferably 1:1 to 2:1 in order to provide good adhesion between the dye and the substrate and inhibit migration of the dye during storage.

20 The coating may also contain other additives, such as curing agents, preservatives, etc., these and other ingredients being described more fully in EP 133011A, EP 133012A and EP 111004A.

The Binder

25 The binder may be any resinous or polymeric material suitable for binding the dye to the substrate which has acceptable solubility in the ink medium, i.e. the medium in which the dye and binder are applied to the transfer sheet. It is preferred however, that the dye is soluble in the binder so that it can exist as a solid solution in the binder on the transfer sheet. In this form it is generally more resistant to migration and crystallisation during storage. Examples of binders include cellulose
30 derivatives; such as ethylhydroxyethylcellulose (EHEC), hydroxypropylcellulose (HPC), ethylcellulose, methylcellulose, cellulose acetate and cellulose acetate butyrate; carbohydrate derivatives, such as starch; alginic acid derivatives; alkyd resins; vinyl resins and derivatives, such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, polyvinyl acetoacetal and polyvinyl pyrrolidone; polycarbonates such as AL-71 from Mitsubishi Gas Chemicals and MAKROLON 2040
35 from Bayer (MAKROLON is a trade mark); polymers and co-polymers derived from acrylates and acrylate derivatives, such as polyacrylic acid, polymethyl methacrylate and styrene-acrylate copolymers, styrene derivatives such as polystyrene, polyester resins, polyamide resins, such as melamines; polyurea and polyurethane resins; organosilicones, such as polysiloxanes, epoxy resins and natural resins, such as gum tragacanth and gum arabic. Mixtures of two or more of the above

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resins may also be used, mixtures preferably comprise a vinyl resin or derivative and a cellulose derivative, more preferably the mixture comprises polyvinyl butyral and ethylcellulose. It is also preferred to use a binder or mixture of binders which is soluble in one of the above-mentioned commercially acceptable organic solvents.

5

The dye or mixture of dyes of Formula (1) has good thermal properties giving rise to even prints on the receiver sheet, whose depth of shade is accurately proportional to the quantity of applied heat so that a true grey scale of coloration can be attained.

The dye or mixture of dyes of Formula (1) also has strong absorbance properties and is
10 soluble in a wide range of solvents, especially those solvents which are widely used and accepted in the printing industry, for example, alkanols, such as i-propanol and butanol; aromatic hydrocarbons, such as toluene, ethers, such as tetrahydrofuran and ketones such as MEK, MIBK and cyclohexanone. Alternatively the mixture of dyes may be dispersed by high shear mixing in suitable media such as water, in the presence of dispersing agents. This produces inks (solvent plus mixture
15 of dyes and binder) which are stable and allow production of solution or dispersion coated dyesheets. The latter are stable, being resistant to dye crystallisation or migration during prolonged storage.

The combination of strong absorbance properties and good solubility in the preferred solvents allows the achievement of good OD of the dye or mixture of dyes of Formula (1) on the
20 receiver sheet. The transfer sheets of the present invention have good stability and produce receiver sheets with good OD and which are fast to both light and heat.

The Substrate

The substrate may be any sheet material preferably having at least one smooth even
25 surface and capable of withstanding the temperatures involved in DDTTP, i.e. up to 400°C for periods up to 20 msec, yet thin enough to transmit heat applied on one side through to the dyes on the other side to effect transfer of the dye onto a receiver sheet within such short periods. Examples of suitable materials are polymers, especially polyester, polyacrylate, polyamide, cellulosic and polyalkylene films, metallised forms thereof, including co-polymer and laminated films, especially
30 laminates incorporating a smooth even polyester receptor layer on which the dye is deposited. Thin (<20 micron) high quality paper of even thickness and having a smooth coated surface, such as capacitor paper, is also suitable. A laminated substrate preferably comprises a backcoat, on the opposite side of the laminate from the receptor layer, which, in the printing process, holds the molten mass together, such as a thermosetting resin, e.g a silicone, acrylate or polyurethane resin, to
35 separate the heat source from the polyester and prevent melting of the latter during the DDTTP operation. The thickness of the substrate depends to some extent upon its thermal conductivity but it is preferably less than 20µm and more preferably less than 10µm.

The DDTTP Process

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According to a further feature of the present invention there is provided a dye diffusion thermal transfer printing process which comprises contacting a transfer sheet comprising a coating comprising a dye or mixture of dyes of Formula (1) with a receiver sheet, so that the coating is in contact with the receiver sheet and selectively applying heat to discrete areas on the reverse side of the transfer sheet whereby the dye on the opposite side of the sheet to the heated areas is transferred to the receiver sheet.

Heating in the selected areas may be effected by contact with heating elements, which can be heated to 200-450°C, preferably 200-400°C, over periods of 2 to 10 msec, whereby the dye mixture may be heated to 150-300°C, depending on the time of exposure, and thereby caused to transfer, substantially by diffusion, from the transfer to the receiver sheet. Good contact between coating and receiver sheet at the point of application is essential to effect transfer. The density of the printed image is related to the time period for which the transfer sheet is heated.

Alternatively, the heating may be effected by means of a laser in which case the dye coat contains an absorber material for absorbing and converting light radiation to heat.

The Receiver Sheet

The receiver sheet conveniently comprises a polymeric sheet material, preferably a white polymeric film and more preferably a material capable of interacting with the interactive functional group(s) defined by Y. The design of receiver and transfer sheets is discussed further in EP 133,011 and EP 133012.

According to a further aspect of the invention, there is provided a thermal transfer printing dye sheet/receiver sheet combination in which the dye sheet comprises a coating comprising a dye or mixture of dyes of Formula (1) and in which the receiver sheet contains at least one polymer capable of interacting with Y.

The invention is further illustrated by the following examples in which all parts and percentages are by weight. The structures of specific dyes suitable for use in the dye sheet of the invention are listed at end of the descriptive part of this specification and the test results given in the Tables have corresponding numbers. It is to be noted that Dyes 1, 2, and 3 are dyes as currently used in commercially available dye sheets.

Example 1

A dye sheet was produced by coating a 6 micron thick poly ethylene terephthalate substrate supplied by Diafoil with a solution containing 1.41% w/w dye and 2.8%w/w poly (vinyl butyral) in

tetrahydrofuran using a K3 wire bar and drying the coating at 110 ° C for 20 seconds to 1.0 µm thickness.

5 A receiver sheet was prepared by coating a Melinex 990 ® substrate with a solution containing 11.1 %w/w of poly (vinyl pyridene) and a cross linked hydroxy functional silicone as release agent, using a K4 wire bar and dried at 140 °C for 3 minutes to give a final coat of 4 µm.

10 Sample prints having an area of 16 cm² were made using a laboratory thermal printer having a TDK L-335H print head operating at a head voltage of 12v for 14 msec. After measuring the optical density using a Macbeth densitometer, the dyed face of a first sample, was covered with a section of plasticised (18% octyl phthalate) PVC wallet making sure the rough surface of the wallet was in contact with the surface of the print. A laboratory tissue was then placed on top of the laminated sample, the next print was placed on the tissue and then covered with a section of plasticised PVC wallet in the same way as before. This procedure was repeated to provide a stack of 10 samples.

15 The final print was then covered with a laboratory tissue and the whole 'stack' of prints was placed between two glass plates, printed faces uppermost, in a humidity oven at 45 °C 85% relative humidity (RH). A 5 kg weight was then placed on top of the whole assembly which was left in the oven for 16 hours.

20 After the 16 hour period had elapsed, the samples were removed from the oven and the PVC wallet was peeled from the print surface. The optical density of the relief image on the contacting surface of the PVC was then measured, at least four different places. The final values used were the average of these four measurements. The recorded re-transfer optical density was then divided by the initial optical density of the print to obtain the percentage (%) re-transfer.

25 The results for various dyes are shown in Table 1.

Further samples were prepared in similar manner except that each sample was printed with four areas using print times of 6.6, 8.8, 10.9 and 13.1 msec. Each area was subjected to a fingerprint from a different person and the samples were then placed in the oven for 16 days. At the end of this period, the samples were examined by eye to determine any defects, each area being given a score of from 0 to 5, a score of 0 indicating the print was unaffected and a score of 5 indicating the quality of the print had been substantially impaired. The scores for the four areas were summated and the final scores are shown in Table 1, lower values indicating better resistance to fingerprint damage.

35

Example 2

Example 1 was repeated (and the samples subjected to the wallet test) for Dyes 1,37,38,39 and 40 except that the dyesheet contained 2.1% dye and 2.1% binder and the receiver contained 11.1% of an amorphous polyester (Vylon 103 ®). The results are shown in Table 2.

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Example 3

Example 2 was repeated except that the polyester in the receiver sheet was replaced with a vinyl pyrrolidone/ vinyl acetate resin. The results are shown in Table 3.

5 Example 4

Example 2 was repeated using poly (vinyl pyridine) in place of the polyester in the receiver sheet. The results are shown in Table 4.

Example 5

10 Example 1 was repeated using Dyes 1, 40, 41, and 42 to provide samples having two areas produced using different print times. The samples were subjected to the wallet test and the results are shown in Table 5

Example 6

15 Example 5 was repeated except that the polyester was replaced in the receiver sheet with a vinyl pyrrolidone/vinyl acetate resin. The results are shown in Table 6.

Example 7Preparation of Dye 4

20 i) Synthesis of 3-cyano-1-(3-hydroxy-2,2-dimethylpropyl)-6-hydroxy-4-methylpyrid-2-one

Ethyl acetoacetate (13g) and ethyl cyanoacetate (11.3g) were added sequentially to a mixture of neo-pentanolamine (25.7g) and water (5cm³) keeping the temperature <10°C. The mixture was then refluxed for 16hrs before drowning into water (50cm³). The aqueous solution was
25 acidified with hydrochloric acid. The pinkish coloured solid which precipitated on stirring for several hours was isolated by filtration, washed with water and dried under reduced pressure. Yield - 13.1g

30 ii) 4-Amino-N,N-bis-(2-hydroxyethyl)benzenesulphonamide (2.6g) was stirred in water (20cm³) and hydrochloric acid (3cm³) added. After cooling to < 10°C a solution of sodium-nitrite (0.8g) in the minimum of water was added keeping the temperature < 10°C. After stirring for 0.25hr excess nitrous acid was destroyed by the addition of sulphamic acid. The resulting diazonium salt solution was added dropwise to a suspension of
35 3-cyano-6-hydroxy-4-methyl-1,3-hydroxy-2,2-dimethylpropylpyrid-2-one (2.4g) in methanol (50cm³). After stirring for 0.5hr the yellow product was isolated by filtration, washed and recrystallised from ethanol to give 4g (80%) of pure product having melting point 268-270°C. (λ_{max} (CH₂CH₂) = 432nm).

Example 8Preparation of Dye 7

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i) 3-(3-Aminophenyl)propionic acid

3-Nitrocinnamic acid (50g) was suspended in ethanol (600cm³) and reduced in the presence of palladium catalyst until no further hydrogen uptake was observed. After filtering the solvent was evaporated under reduced pressure to give the pure product in quantitative yield as a brown oil which slowly crystallised.

ii) 3-(3-Aminophenyl)propionic acid (0.83g) was added to a solution of hydrochloric acid (3cm³) in water (20cm³) at 0C. A solution of sodium nitrite (0.35g) in the minimum of water was then added dropwise keeping the temperature below 5C. After stirring for 0.25hrs the excess nitrous acid was destroyed with sulphamic acid and the diazonium salt solution filtered before adding slowly to a cooled solution of 1-carboxymethyl-3-cyano-6-hydroxy-4-methylpyrid-2-one (1.04g) in methanol (50cm³). After stirring for 1hr the yellow product was filtered off washed with water and methanol and dried (81%). mp258-60C, λ max(CH₂CH₂) 434nm.

Example 9

Preparation of Dye 8

4-(4-Cyano-3-methylisothiazol-5-ylazo)-N,N-bis-(2-hydroxyethyl)-3-toluidine (3.45g) and glutaric anhydride (5.0g) were refluxed in pyridine (20cm³) until TLC showed complete reaction. The cooled solution was poured into water (200cm³) and acidified with hydrochloric acid. The precipitated product was filtered off, washed with water and dried under reduced pressure to give analytically pure product (82%).

Example 10

Preparation of Dye 10

This product was synthesised in analogous manner to Example 9 replacing the 4-(4-cyano-3-methylisothiazol-5-ylazo)-N,N-bis-(2-hydroxyethyl)-3-toluidine by N,N-bis-(2-hydroxyethyl)- 4-(5-nitrobenzoiisothiazol-7-ylazo)-3-toluidine (4.05g) and the glutaric anhydride by succinic anhydride (4.4g).

Example 11

Preparation of Dye 11

To a solution of N,N-Bis-(2-hydroxyethyl)-4-formyl-3-toluidine (3.85g) and malononitrile (1.14g) in ethanol (20cm³) was added a few drops of piperidine. The solution was refluxed for 0.5hr, cooled and poured into water (150cm³). The resulting product was filtered off washed and dried. Reaction as described in Example 9 using succinic anhydride yielded a yellow solid (86%)

Example 12

Preparation of Dye 13

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i) Aniline (37.2g), 3-chloropropan-1-ol (113.4g), and calcium carbonate (60g) in water (500cm³) were refluxed for 30hrs. The resulting mixture was filtered and the filtrate separated into an oil and a water layer. the oil was dissolved in dichloromethane and the solvent removed to leave N,N-bis(3-hydroxypropyl)aniline as a brown oil.

5

ii) N,N-bis(3-hydroxypropyl) aniline (10.46g) was dissolved in hydrochloric acid (20cm³) at 0-5C and sodium nitrite(3.45g) in water(15cm³) was added dropwise. The mixture was stirred for 1hr, water (10cm³) was added, made alkaline with sodium carbonate, separated in to an oil and water layer. The oil was dissolved in dichloromethane and the solvent removed to leave

10

iii) Iron powder (6.72g), N,N-bis(3-hydroxypropyl)-4-nitrosoaniline (10g) and hydrochloric acid(20cm³) in methanol (120cm³) were refluxed for 2hrs. The resulting mixture was made alkaline with sodium carbonate, filtered and the solvent removed to leave N,N-bis(3-hydroxypropyl)-4-aminoaniline as a brown solid.

15

iv) Ammonium persulphate(9.13g) was added portionwise with stirring to a mixture of N,N-bis(3hydroxypropyl)-4-aminoaniline(4.48g), 3-cyano-6-hydroxy-4-methyl-1-neopentyl(4.73g), sodium carbonate (4.24g) and acetone (30cm³) in water (cm), stirred for 1hr, acetone removed and the resulting solution was extracted with ethyl acetate (3x200cm³) and the combined extracts dried over magnesium sulphate, filtered and solvent removed to leave the title compound. m.p.166C, λ_{\max} 569nm (methanol). Mmax 25370

20

Example 13

Preparation of Dye 17

The diethylester (1.5g, 0.003mol) was dissolved in methanol (30cm³) and 48% sodium hydroxide solution (0.5cm³) added, reaction stirred and refluxed for 1hr. The mixture was poured into water (150cm³) acidified with concentrated HCl and precipitated solid filtered off, washed with water and dried (1g, 74%). λ_{\max} (MeOH) 524nm

Example 14

Preparation of Dye 24

30

1,4-Diaminoanthraquinone (3.6g, 0.015mol) and acrylic acid (30cm³) were stirred at 100-110C for 1phrs, allowed to cool and diluted with methanol (45cm³). After cooling to room temperature, the product was filtered off, washed with methanol and dried (4.9g, 86%). λ_{\max} (MeOH) 570nm.

35

Example 15

Preparation of Dye 26

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Using diaminoanthrarufin in the procedure described in Example 14 above gave the required product. λ_{\max} (MeOH) 660+610nm.

Example 16

5 Preparation of Dye 31

The procedure as described for Example 9 was followed except the 4-(4-cyano-3-methylisothiazol-5-ylazo)-N,N-bis(2-hydroxyethyl)-3-toluidine was replaced by 4-(4-ethylhydroxyphenylazo)-N,N-bis(2-hydroxyethyl)-3-aminoacetanilide to give the title compound, λ_{\max} 464nm (water).

10

Example 17

Preparation of Dye 35

4-(4-Cyano-3-methylisothiazol-5-ylazo)-N,N-bis-(3-ethoxycarbonylpropyl)-3-toluidine (1.4g), 15 methanol (30cm³) and sodium hydroxide liquor (0.5cm³, 40%w/w) were stirred and heated to reflux for 1hr when TLC showed complete hydrolysis. The cooled mixture was poured into water (150cm³) and the solution acidified with hydrochloric acid. The precipitated product was isolated by filtration, washed with water and dried to give 0.96g of product mp 166-9C. λ_{\max} (acetone) 548nm.

Example 18

20

Preparation of Dye 36

To N,N-dicarboxyethyl-3-toluidine (2.51g, 0.01mol) and dimethylformamide (5cm³) was added tetracyanoethylene (1.28g, 0.01mol) over 15 mins; keeping the temperature below 40C. Reaction mixture heated to 55C for phr, solution cooled, poured into ice/water to give a sticky solid. 25 Solid purified by column chromatography (silica; ethylacetate) to give a black solid (1g, 28%). λ_{\max} (MeOH) 524nm.

30

35

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TABLE 1

	DYE	OPTICAL DENSITY	% RE- TRANSFER	FINGERPRINT SCORE
5	1	0.85	25.9	8
	2	0.63	17.5	20
	3	0.9	21.1	10
	4	0.6	3.3	-
	5	0.43	0	5
10	6	0.71	1.4	6
	7	1.23	0.8	4
	8	1.3	0.8	2
	9	0.7	0	13
	10	0.93	0	2
15	11	1.29	0	1
	12	0.72	1.4	3
	13	0.86	2.3	-
	14	0.6	1.7	-
	15	0.6	21.7	1
20	16	0.62	0	1
	17	0.96	0	9
	18	0.17	0	5
	19	0.83	0	11
	20	0.91	0	6
25	21	1.01	2.0	3
	22	0.55	0	3
	23	0.35	0	5
	24	0.46	0	7
	25	0.55	0	4
30	26	0.53	0	5
	27	0.64	0	-
	28	0.24	0	11
	29	0.55	0	2
	30	1.47	0.7	1
35	31	0.62	0	0
	32	0.41	0	7
	33	0.76	0	11
	34	1.48	2.03	-
	35	1.6	0.63	-
	36	1.3	0.8	-

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TABLE 2

	DYE	ORIGINAL OD	TRANSFER OD	% LOSS
5	1	2.42	0.30	12.4
	37	1.24	0.09	7.3
	38	1.60	0.07	4.4
	39	2.05	0.26	12.6
	40	1.77	0.08	4.5
10				

TABLE 3

	DYE	ORIGINAL OD	TRANSFER OD	% LOSS
15	1	2.16	0.96	44.4
	37	1.82	0.00	0.0
	38	2.03	0.00	0.0
	39	2.18	0.05	2.3
	40	2.06	0.00	0.0
20				

TABLE 4

	DYE	ORIGINAL OD	TRANSFER OD	% LOSS
25	1	1.66	0.49	29.5
	37	1.39	0.00	0.0
	38	1.65	0.00	0.0
	39	1.89	0.10	5.3
	40	1.73	0.00	0.0
30				

35

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24

TABLE 5

	DYE	PRINT TIME mS	ORIGINAL OD	TRANSFER OD	% LOSS
5	1	8.5	1.20	0.29	24.2
	1	10.6	-	-	-
	40	8.5	0.26	0.02	7.70
	40	10.6	0.67	0.02	2.99
10	41	8.5	0.28	0.01	3.60
	41	10.6	0.68	0.01	1.47
	42	8.5	0.25	0.01	4.10
	42	10.6	0.64	0.01	1.56

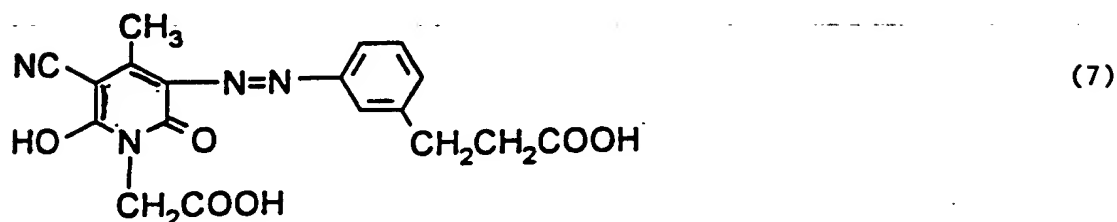
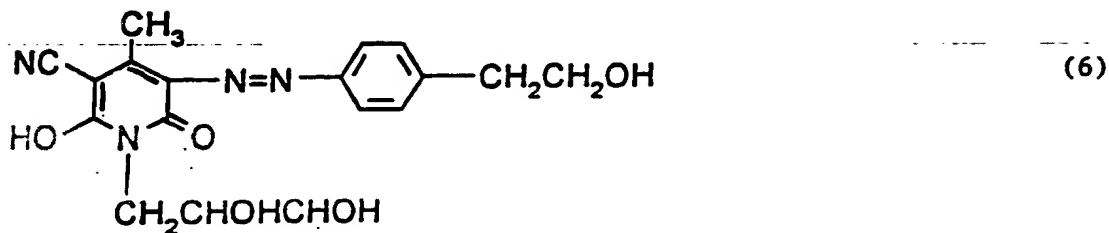
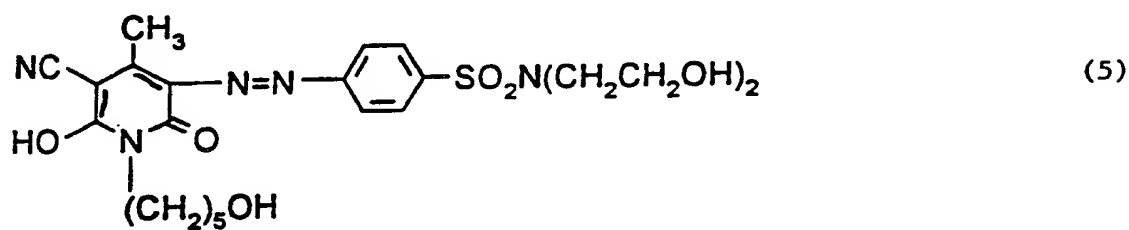
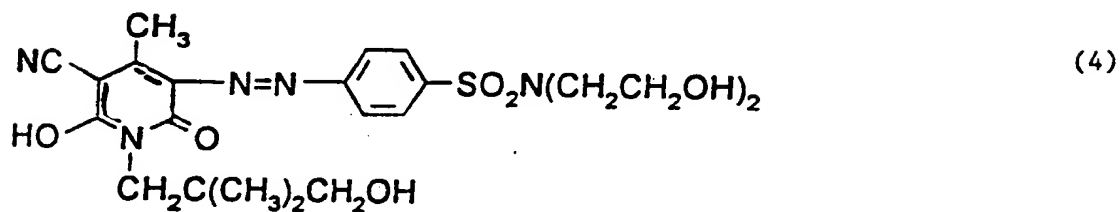
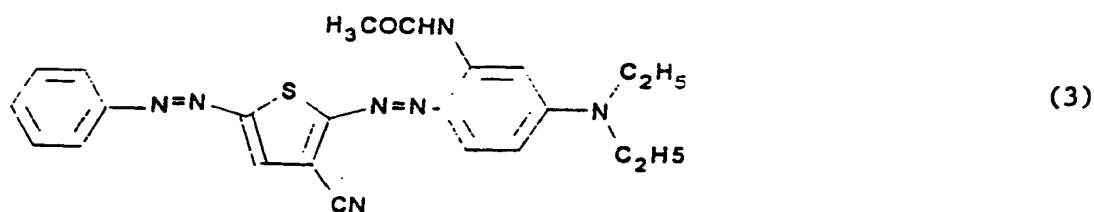
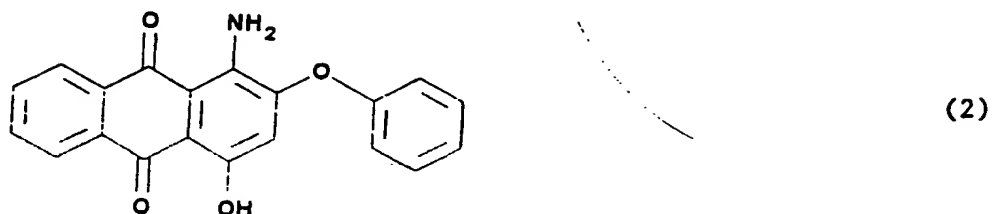
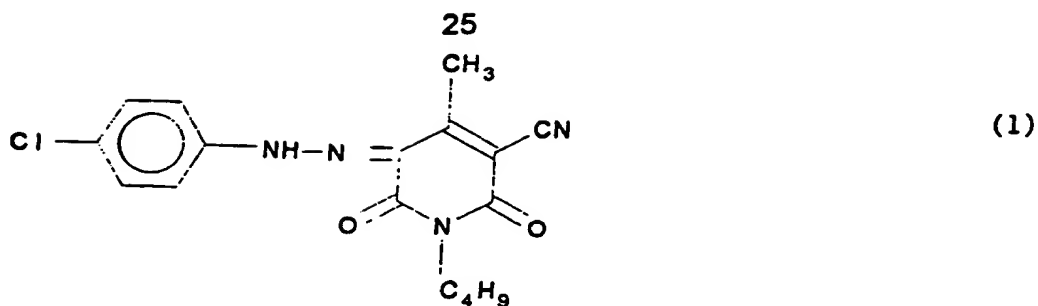
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TABLE 6

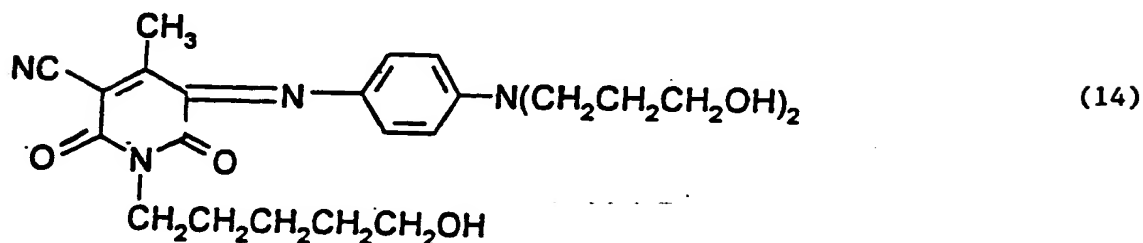
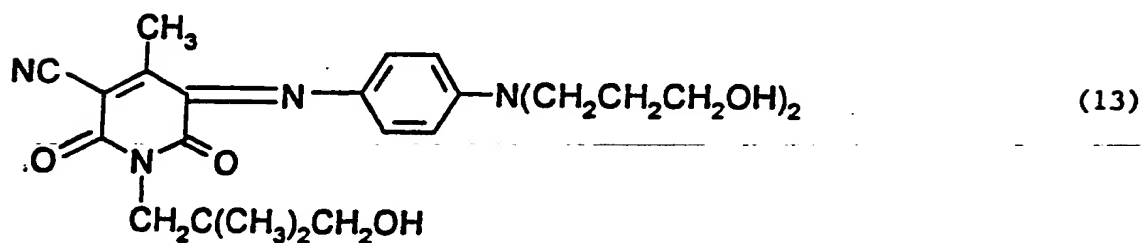
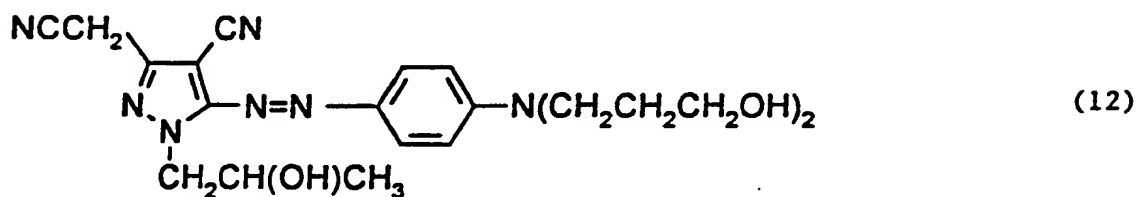
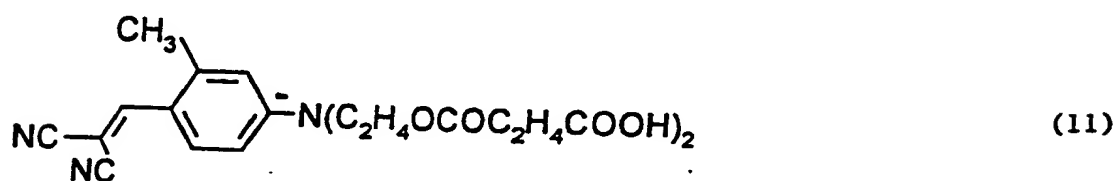
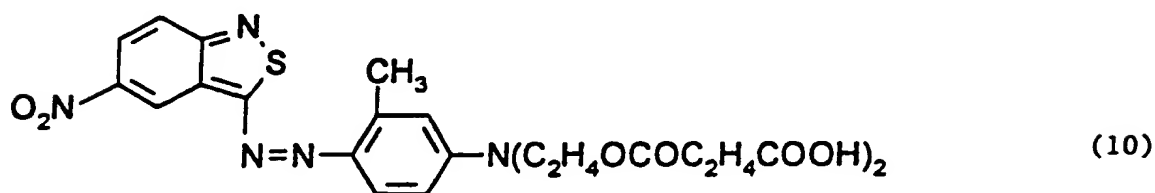
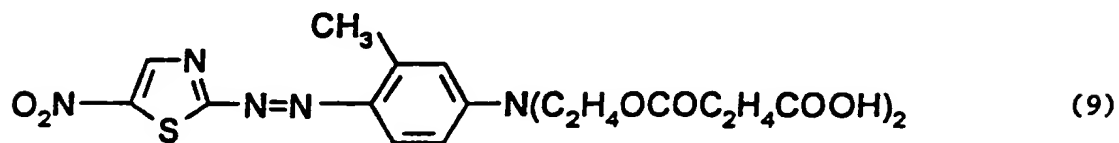
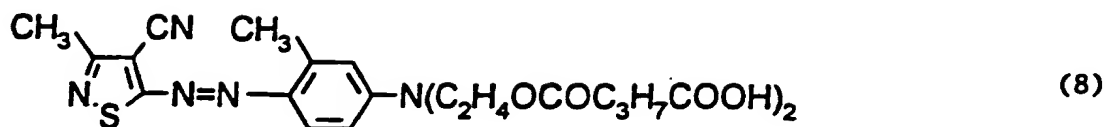
	DYE	PRINT TIME mS	ORIGINAL OD	TRANSFER OD	% LOSS
20	1	8.5	0.93	0.64	68.90
	1	10.6	1.86	0.63	33.90
	1	12.7	2.04	0.97	47.50
	40	8.5	0.37	0.00	0.00
25	40	10.6	0.90	0.00	0.00
	40	12.7	1.48	0.00	0.00
	41	8.5	0.36	0.00	0.00
	41	10.6	0.91	0.00	0.00
30	41	12.7	1.25	0.00	0.00
	42	8.5	0.48	0.00	0.00
	42	10.6	1.00	0.01	1.00
	42	12.7	1.35	0.02	1.50

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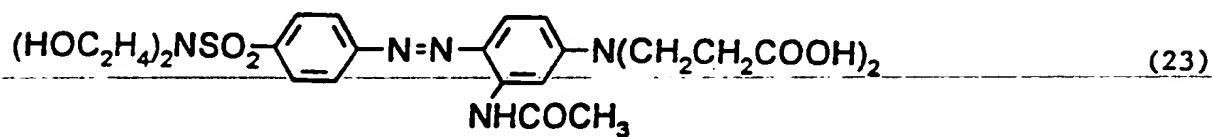
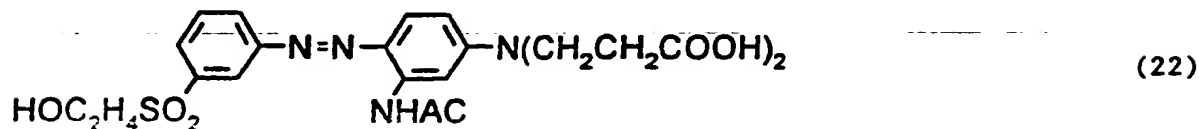
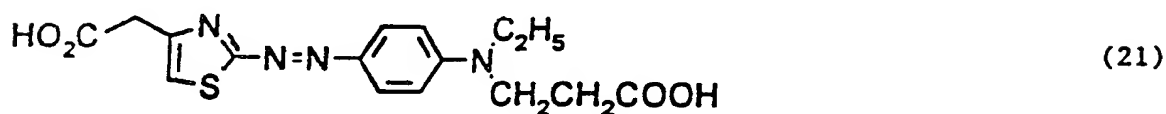
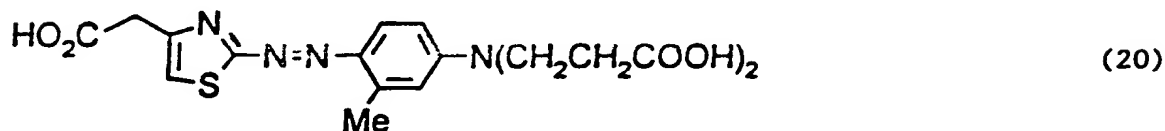
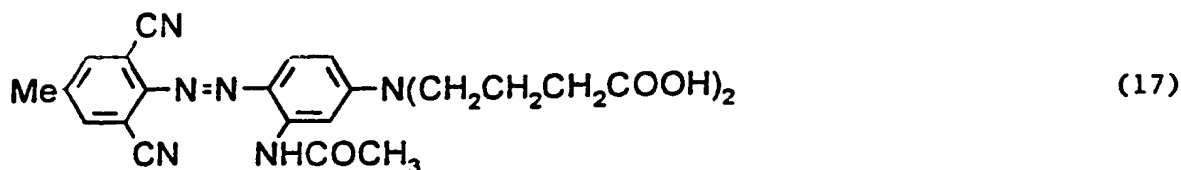
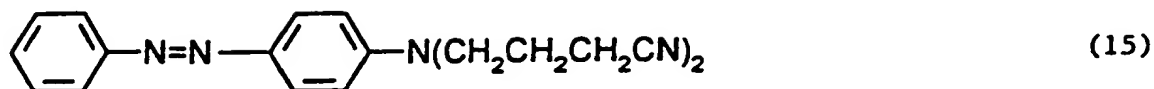
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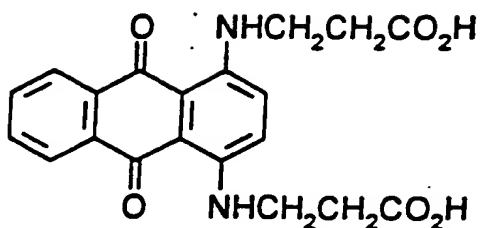
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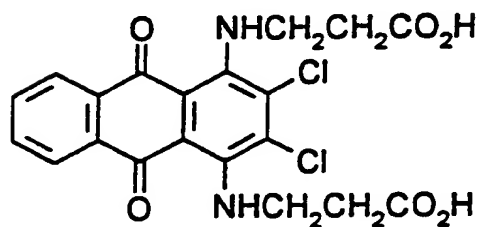
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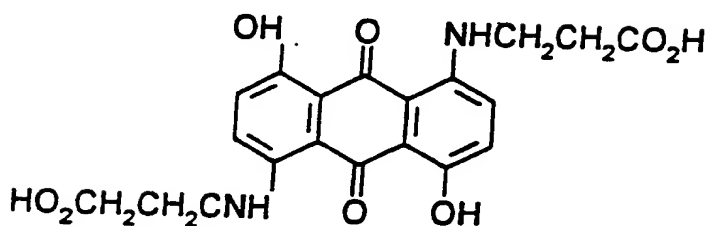
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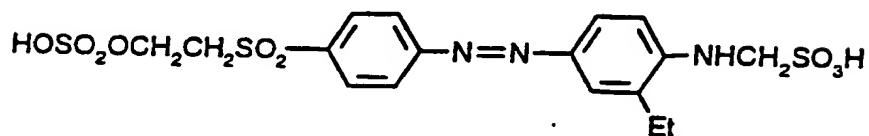
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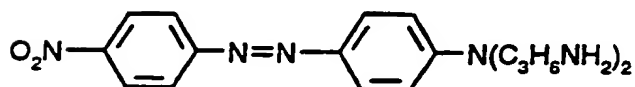
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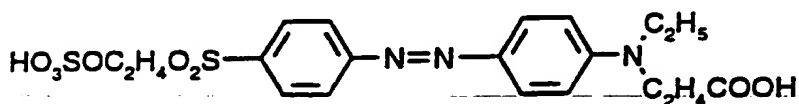
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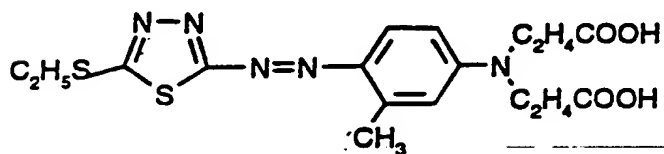
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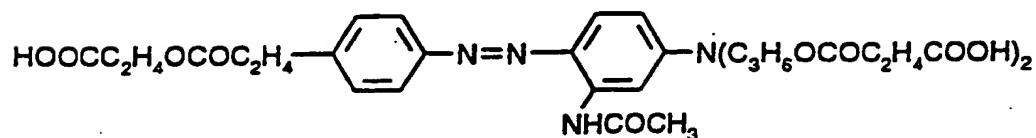
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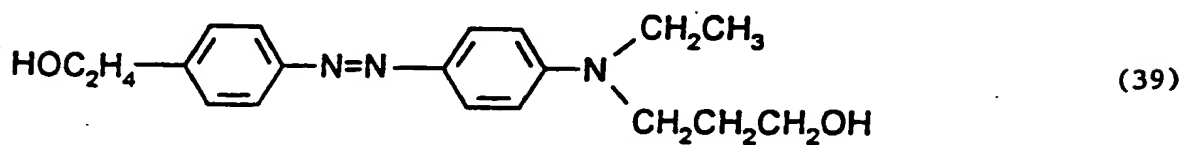
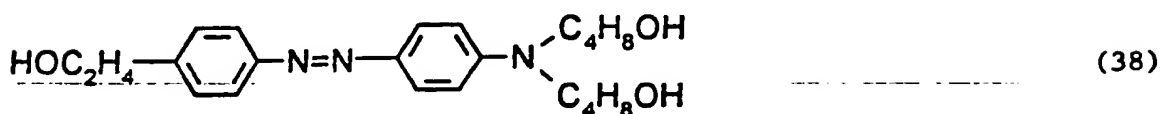
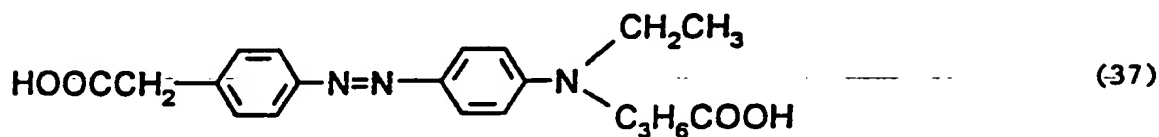
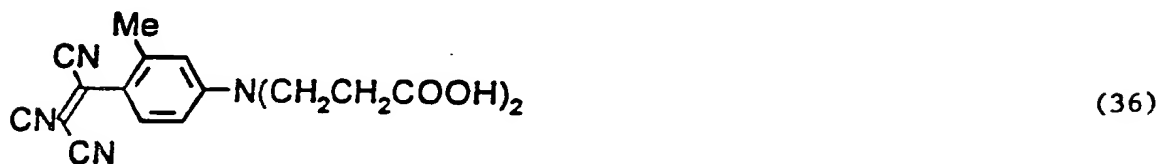
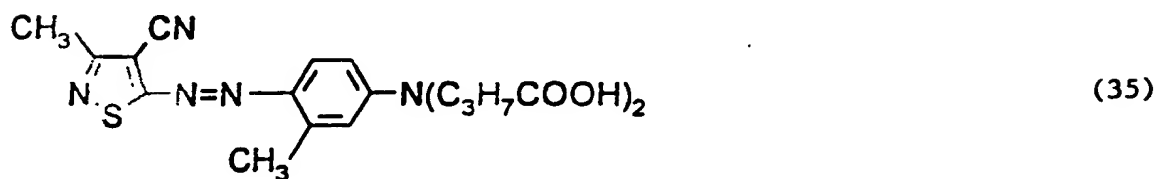
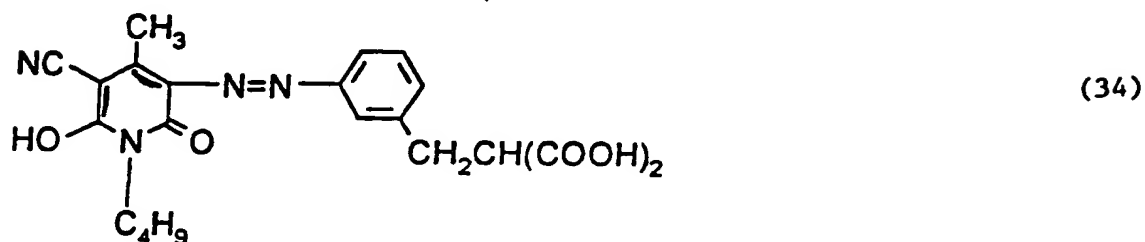
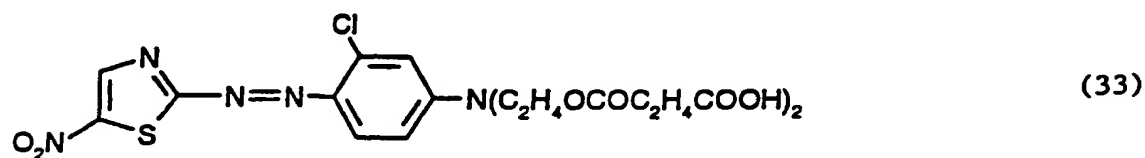
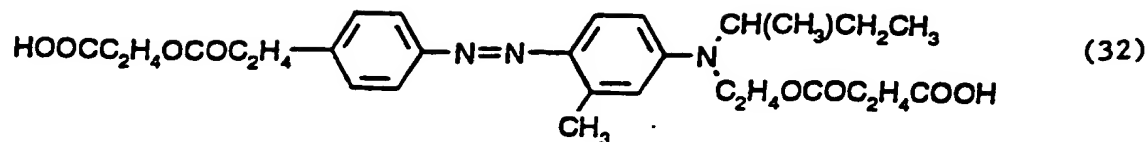
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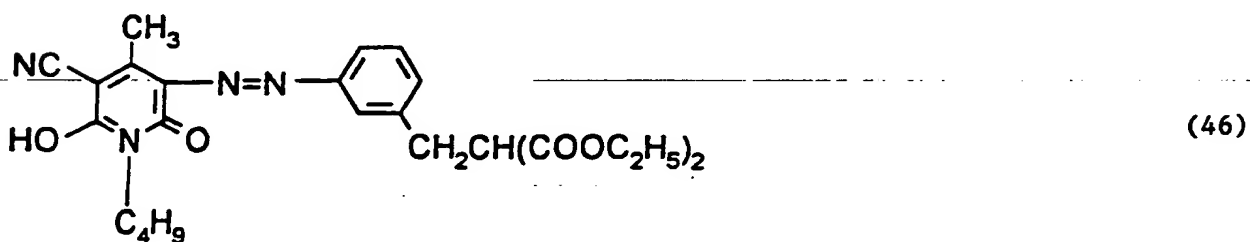
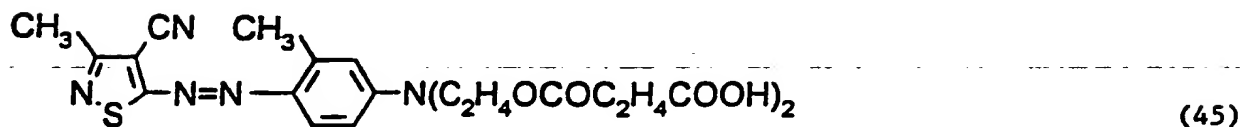
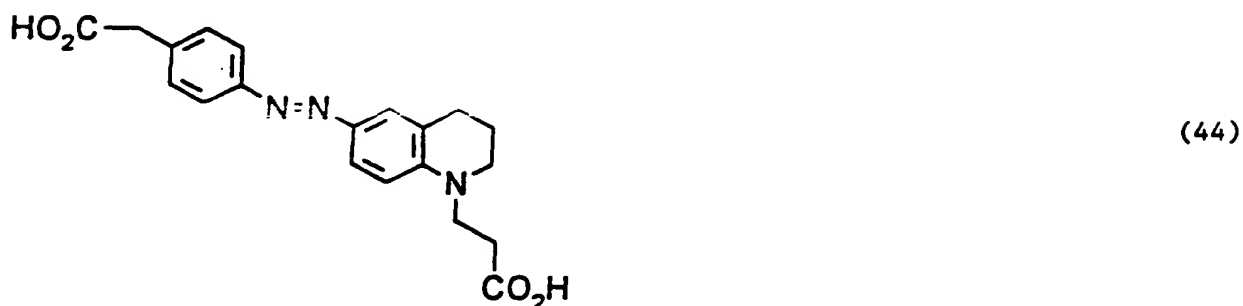
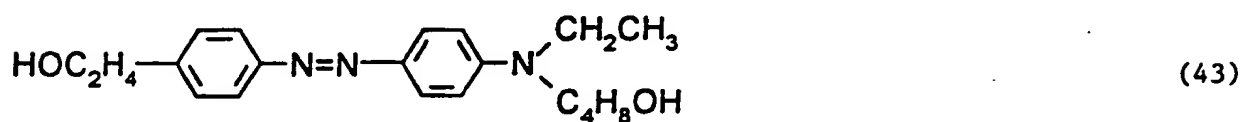
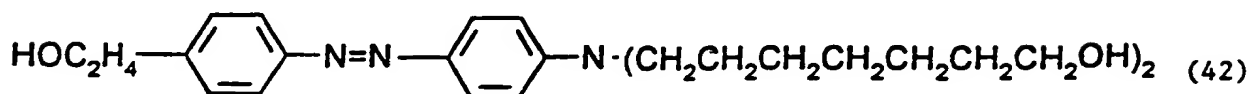
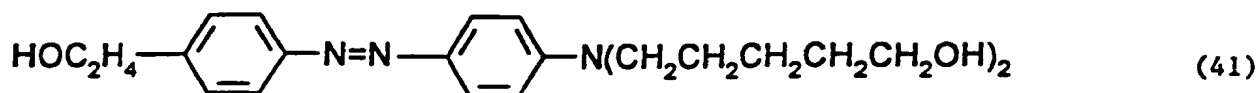
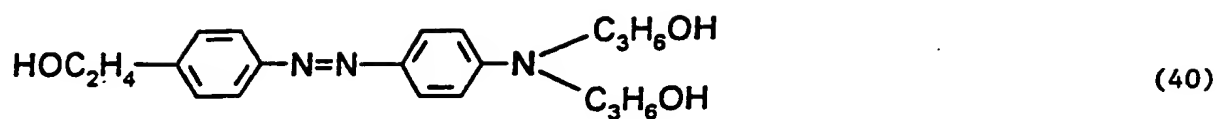
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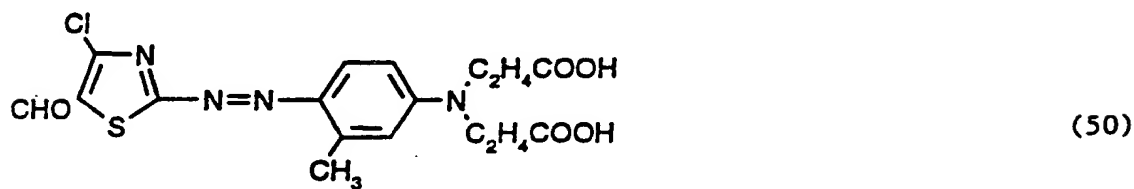
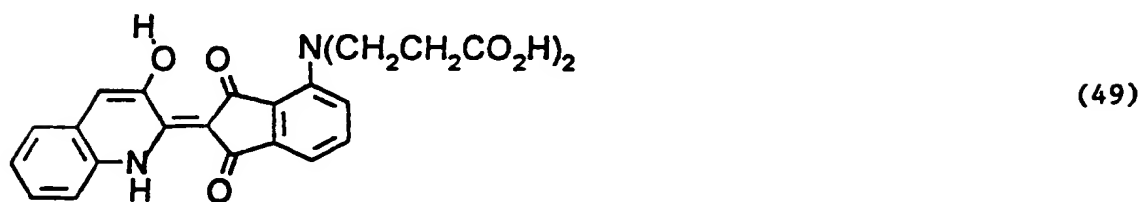
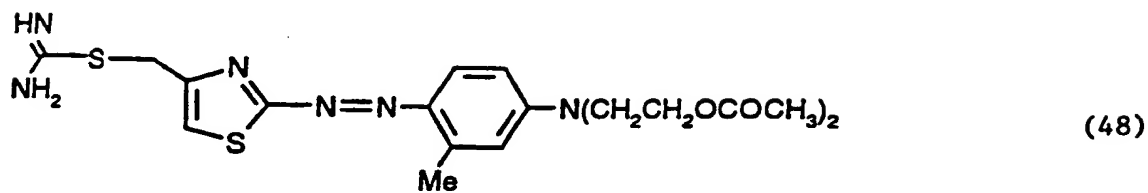
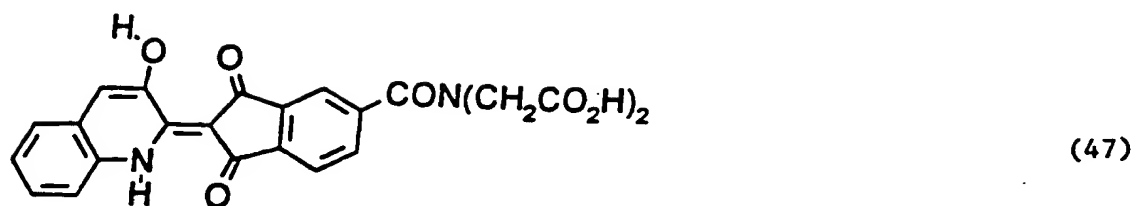
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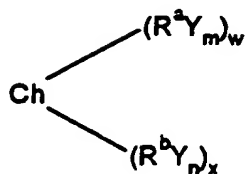
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Claims

1. A thermal transfer dye sheet comprising a substrate having a coating comprising a dye of Formula (1):



Formula (1)

in which:

Ch is a chromogen as herein defined

Ra and Rb each independently is a spacer group

Y is an interactive functional group

w and x each independently is 0 or an integer equal to or greater than 1, and

m and n each independently is an integer equal to or greater than 1, provided that w and x are not both equal to 0 and when one of w or x is 0 at least one of m and n is equal to or greater than 2.

2. A thermal transfer dye sheet according to claim 1, in which the interactive functional groups are the same or different.

3. A thermal transfer dye sheet according to claim 2, in which at least one of the interactive functional groups contains at least one hydrogen atom.

4. A thermal transfer dye sheet according to claim 1 or 2, in which the interactive functional groups are selected from the group comprising OH, NH₂, NHR, NR₂, COOH, CONH₂, NHCOR, CONHR, SO₂NH₂, SO₂NHR, SO₃H, NHCONH₂, NHCONHR, =NOH, and PO₃H,

5. A thermal transfer dye sheet according to claim 4, in which the interactive functional groups are selected from the group comprising OH, NH₂, NHR, NR₂, COOH, CONH₂, CONHR, SO₂NH₂, SO₂NHR and =NOH.

6. A thermal transfer dye sheet according to claim 4 in which the interactive functional groups are selected from the group comprising NH₂, NHR AND NR₂.

7. A thermal transfer dye sheet according to claim 4 in which the interactive functional groups are selected from the group comprising OH and COOH.

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8. A thermal transfer dye sheet according to claim 4 in which the interactive functional groups are COOH.

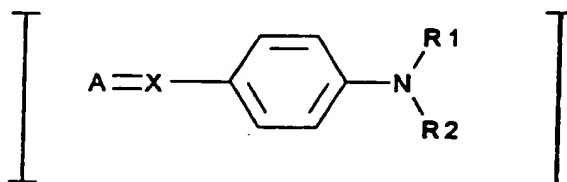
9. A thermal transfer dye sheet according to any preceding claim, in which the spacer groups each comprise an atom or group of atoms connected to Ch by at least one sigma bond and to Y by at least one sigma bond.

10. A thermal transfer dye sheet according to claim 9, in which the spacer groups contain at least one of a carbon, silicon or sulphur atom.

11. A thermal transfer dye sheet according to claim 10, in which the spacer groups contain at least two carbon atoms.

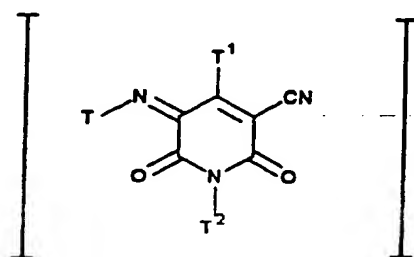
12. A thermal transfer dye sheet according to claim 10, in which the spacer groups contain from 3 to 10 carbon atoms.

13. A thermal transfer dye sheet according to any preceding claim, in which the chromagen is an optionally substituted group of Formula (2)



Formula (2)

or an optionally substituted group of Formula (2B)



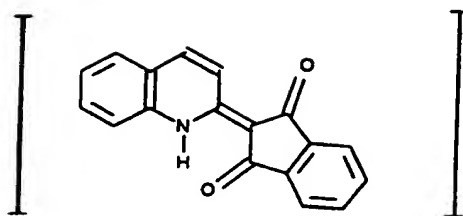
Formula (2B)

in which T is an A¹ - NH or optionally substituted phenyl (such as optionally substituted mono- or dialkylaminophenyl), T¹ is optionally substituted C¹ - C¹² alkyl or optionally substituted aryl and T² is optionally substituted alkyl;

or an optionally substituted group of Formula (3)

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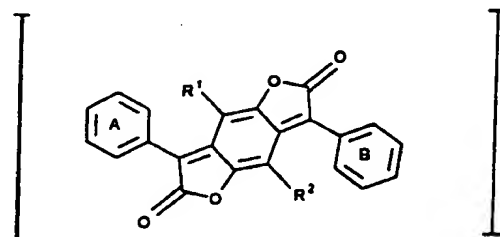
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Formula (3)

10 an optionally substituted group of Formula (4)

15



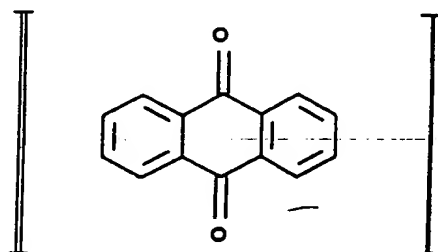
Formula (4)

20

in which rings A and B are optionally substituted and R1 and R2 each independently is H, alkyl, alkoxy or halogen;

25 or an optionally substituted group of Formula (5):

30



Formula (5)

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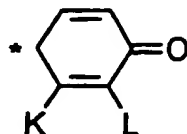
in which

X is -C(R)- or N and R is H, CN or COOalkyl; and

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A is A1 - N in which A1 is the residue of a diazotisable aromatic or heteroaromatic amine or A is selected from an optionally substituted group of Formula (6)

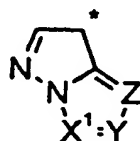
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Formula (6)

10 in which K and L each independently is -CN, NO₂, -Cl, -F, -Br, C₁₋₆ alkyl, C₁₋₆ alkoxy, -NHCOC₁₋₆ alkyl, -NHCOphenyl, -NHSO₂ alkyl, NHSO₂phenyl or aryloxy, or K and L together with the carbon atoms to which they are attached form a 5- or 6- membered carbocyclic or heterocyclic ring; or an optionally substituted group of Formula (7):

15

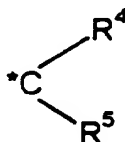


Formula (7)

20

in which X', Y and Z each independently is N or C-R³ in which R³ is H, CN, alkyl, alkoxy, cycloalkyl, aryl, aralkyl, aryloxy, or amino; or an optionally substituted group of Formula (8)

25



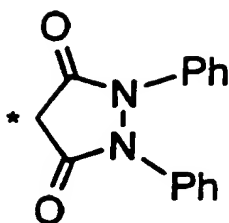
Formula (8)

30

in which R⁴ and R⁵ each independently is an electron withdrawing group or R⁴ and R⁵ may be joined to form a heterocyclic ring such as

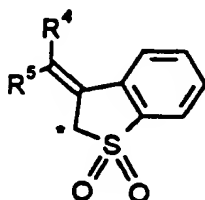
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or an optionally substituted group of Formula 9:

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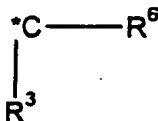


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Formula (9)

in which R⁴ and R⁵ are as hereinbefore defined; or an optionally substituted group of Formula 10

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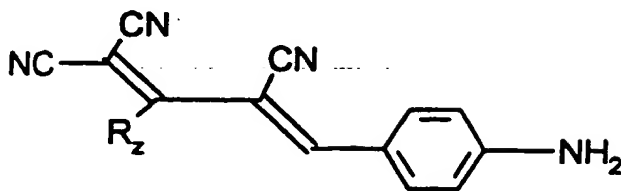


25

Formula (10)

in which R³ is as hereinbefore defined and R⁶ is alkenyl or

30



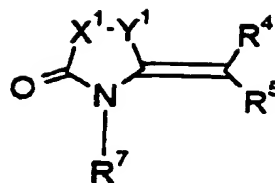
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in which R² is NH₂ phenyl or succinamido;

or an optionally substituted group of Formula (11)

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37



Formula (11)

in which X¹ and Y¹ are both C and R⁴ and R⁵ are as hereinbefore defined and R⁷ is H, alkyl or aryl,

10 where * shows the point of attachment to the double bond in Formula (5).

14. A thermal transfer dye sheet according to claim 13, in which A¹ is selected from the group comprising phenyl, naphthyl, thiazolyl, isothiazolyl, benzothiazolyl, pyrazolyl, thiadiazolyl, imidazolyl, thienyl, pyridyl and pyridoisothiazolyl each of which may be substituted.

15 15 A thermal transfer dye sheet according to claim 13, in which the chromagen contains an alpha-branched N-alkyl group.

16. A thermal transfer dye sheet according to any preceding claim in which the dye has a melting point in the range from 20°C to 200 °C.

20 17 A thermal transfer dye sheet according to any preceding claim and further comprising a material for absorbing and converting light radiation to heat.

18. A thermal transfer dye sheet / receiver sheet combination in which the dye sheet comprises a coating comprising a dye or mixture of dyes of Formula (1) and in which the receiver sheet contains a polymer having at least one group capable of interacting with Y.

25 19. A thermal transfer dye sheet / receiver sheet combination according to claim 18, in which the polymer contains at least one group selected from =N, NR₂, NRH, NH₂, OH, COOH or SO₃H.

30

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INTERNATIONAL SEARCH REPORT

National Application No

PCT/GB 96/01027

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B41M5/38 B41M5/00 D06P5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 159 971 (MITSUBISHI CHEM IND) 11 December 1985 see page 1, line 22-37 see page 1, line 41 - page 20, line 20 see page 20, line 55 - page 29, line 8 ---	1-19
X	US,A,3 940 246 (DEFAGO RAYMOND ET AL) 24 February 1976 see column 1, line 18 - column 7, line 68 see examples ---	1-17
X	FR,A,2 136 457 (CIBA GEIGY AG) 22 December 1972 see page 1, line 20 - page 5, line 40 see examples ---	1-17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 July 1996

Date of mailing of the international search report

- 7. 08. 96

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INTERNATIONAL SEARCH REPORT

 Inter Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE,A,38 29 918 (FUJI PHOTO FILM CO LTD) 16 March 1989 see page 3, line 45 - page 4, line 59 see page 5, line 55 - line 56 see dyes 15,16 ---	1-17
X	EP,A,0 613 783 (DAINIPPON PRINTING CO LTD) 7 September 1994 see page 2, line 3 - line 53 see page 3, line 15 - page 4, line 9 see Table 1, Example 1-2 see Examples , Table 8 ---	1-17
X	EP,A,0 400 706 (AGFA GEVAERT NV) 5 December 1990 see page 3, line 34 - page 4, line 54 see table 1, dyes 1.51, 1.66 ---	1-17
X	EP,A,0 327 077 (DAINIPPON PRINTING CO LTD) 9 August 1989 see page 2, line 55 - page 3, line 40 see Table 1, No. 5 see Example 1, Table 2 ---	1-17
X	EP,A,0 229 374 (EASTMAN KODAK CO) 22 July 1987 see page 3, line 25 - page 4, line 14 see Compound No. 7 see Example 3, Table 5 ---	1-17
X	EP,A,0 582 324 (DAINIPPON PRINTING CO LTD) 9 February 1994 see page 2, line 51 - line 58 see page 13, line 55 - page 16, line 20 see Table D1, Nos. 2,14,20, Table D2, Nos. 2,14 see example D ---	1-17
X	EP,A,0 526 170 (MITSUI TOATSU CHEMICALS) 3 February 1993 see page 2, line 1 - page 3, line 36 see example 5 ---	1-17
1 X	EP,A,0 468 380 (SONY CORP) 29 January 1992 see page 2, line 28 - line 57 see EXAMPLE 11, DYE 11 ---	1-17

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/01027

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 350 731 (WILLIAMS LINDA K ET AL) 27 September 1994 see column 3, line 55 - column 4, line 7 see examples 4,6-8 ---	1-17
X	EP,A,0 001 068 (FROMSON H A) 21 March 1979 see page 16, line 1 - line 6 see dye Red 17 ---	1-17
P,X	EP,A,0 655 345 (FUJI PHOTO FILM CO LTD) 31 May 1995 see page 2, line 26 - page 3, line 26 see example dyes I-11, I-22, IV-6, IV-41 -----	1-18

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Original Application No

PCT/GB 96/01027

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